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Functionalized Coatings by Electrospinning for Anti-oxidant Food Packaging

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Abstract

The development of advanced formulations used for food packaging applications, which behave as protection or preservation materials and improve consumers' health offers a route to reduced food wastage. The present study deals with investigations on the possibility of obtaining functionalized coatings by electrospinning of poly(ε-caprolactone), a synthetic biodegradable polymer together with vitamin E (α-tocopherol), selected as plant-based phenolic antioxidant. In this approach electrospinning allows the production of high surface area materials and thus offering an increased antioxidant activity. The electrospun fibres of poly(ε-caprolactone)/vitamin E were obtained, studied and their antioxidant properties were evaluated by measuring the fibre reactivity with 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical. The potential for extending the shelf-life of food products by using this approach is discussed.

Peer-review under responsibility of the scientific committee of the International Conference on Sustainable and Intelligent Manufacturing

Keywords: food packaging; electrospinning; anti-oxidant.

1. Introduction

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Food packaging is one of the major users of plastic materials and enables the self-service in the supermarket system. The packaging provides protection from the environment and the customer, it offers tampering resistance, but at the same time it allows the customer to view the product within. It protects the food from the shopper. It is especially important to prevent the ingress of bacteria which will lead to food spoilage and the necessity for it to be disposed. Packaging for meat products is especially important both to provide clear packaging for visual inspection and a barrier between the meat and the external environment. The qualities of packaging need to prevent oxidative degradation reactions of fats, proteins and pigments which will lead to degradation of the meat and affect its appearance, leading to customer rejection and greater waste. Lately, the use of active atmospheres and adding function to the packaging materials are discussed extensively.

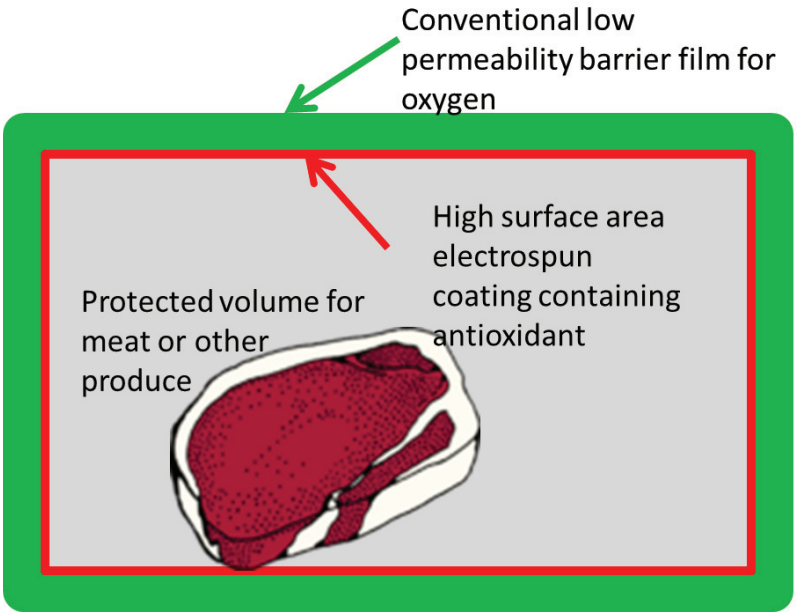


Fig. 1: Schematic representation of the design features of the anti-oxidant packaging considered in this work.

Packaging may offer additional routes for protecting food, as for example in the work of Lagaron et al on in-built temperature control [1] and the recent work of Krepker et al on packaging with antimicrobial functionality [2]. Of course the packaging already has the function of conveying nutrition facts and other information about food being offered for sale. In this work, the aim was to add antioxidant function. Thus, any oxygen which diffuses through the packaging material will be scavenged resulting in extending the shelf-life. The current status with respect to packaging for meat is detailed in the work of Fang et al [3]. Selection of materials for food packaging which comes in to contact with food is strongly regulated. Within the European Union the framework Regulation (EC) No. 1935:2004 covers this area. In the USA, this area is covered by the Food and Drug Administration and in particular by Code of Federal Legislation (CFR): 21 CFR 174 - 21 CFR 190.

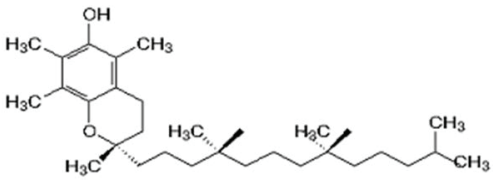
In setting out to design an anti-oxidant food packaging coating material we have not necessarily plan to develop new materials but rather to exploit materials already approved for food contact (Figure 1). We have decided to develop a coating system for existing high performance barrier films, some of which are based on nanocomposites [4] and all the features of the existing packaging such as good mechanical strength, low permeability for oxygen and optical clarity to be kept. Because it is desirable that the anti-oxidant properties to be effective over a period of time, we need to adapt the approaches taken for a slow release. As a consequence the anti-oxidant is incorporated in to a polymer matrix. Thus a high surface area coating is generated using electrospun fibres. The electrospinning technique [5] readily produces microscale to nanoscale sized polymer fibres, through the application of a high voltage to a polymer solution or melt contained within a spinneret. The high voltage induces a deformation of the

droplet at the needle tip from which a polymer jet is extruded and stretched towards a grounded target electrode. On transit from the spinneret tip to the collector, the jet is stretched down to a micro- to nano- scale polymer fibre and solvent is removed or solidification occurs depending on whether the process began with a solution or molten state, thereby leaving a solid polymer fibre on the collector. Without additional control, electrospinning naturally generates random mats of fibres on the surface of the substrate, providing a high accessibilty surface layer.

2. Experimental

2.1 Materials

Poly(ε-caprolactone) (PCL) with a Mw of 80,000 Daltons was selected as the carrier for the antioxidant. This provides a level of oxygen permeability which can facilitate the respiration of the product and in the same time the anti-oxidant effect of the Vitamin E. Poly(ε-caprolactone) is widely used as a biodegradable polymer in medical devices. When suitable high performance biopolymer based films are available this biodegradable coating can be used to prepare compostable food packaging [6].



I Chemical structure of α-tocopherol

α-Tocopherol as form of vitamin E wassupplied by Sigma-Aldrich [I] is a lipid-soluble vitamin, with well-known antioxidant properties, as a consequence of the phenolic OH group, which reacts effectively with free radicals by H-atom transfer.

2.1. Electrospinning

Solutions of 20 wt% Poly(ε-caprolactone) were prepared using 1,2-Dichloroethane as solvent and varying amounts of Vitamin E 0 – 17 wt % with respect to the Poly(ε-caprolactone). Vitamin E is a viscous liquid in the bulk at room temperature. A conventional horizontal electrospinning set-up was used, with a flat aluminium collector electrode. Electrospinning was performed with a high voltage of 15 kV and a distance from needle to collector of 15 cm which gives an electric field of $150Vm^{-1}$. The solution was contained within a glass syringe with a 0.62mm inner diameter needle. The syringe was mounted in a controlled syringe pump with a feed rate of 0.179 ml/min.

2.2 Viscosity Measurements

A Bohlin constant stress rheometer with cone-plate geometry was used to measure the variation of solution viscosity as a function of shear rate and Vitamin E content at room temperature.

Scanning electron microscopy (SEM) was performed on sections of the fibres produced. The microscopy was performed using a Cambridge Instruments SEM360 in high vacuum mode with an accelerating voltage of 20 kV. Fibres were coated with gold prior to examination. Fibres were selected at random from the micrographs obtained and measurements were made using the software ImageJ.

2.3 Anti-oxidant Activity

The antioxidant properties of the obtained fibers were studied by DPPH radical scavenging assay, using the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) [7-9]. 10-20 mg of collected fibers with various vitamin E content (1 wt%, 2 wt%, 5 wt%, 10 wt% and 20 wt%) were placed in a flask containing 2 mL of methanol and was stirred for 3 h at room temperature (200C). The supernatant solution obtained was analyzed for DPPH radical scavenging activity. 2 mL of methanolic solution of DPPH (0.06 mM) was mixed with 500 µL of supernatant/solution. The control was obtained using 500 µL of methanolic solution without the presence of the fibers. The mixture was vortexed vigorously and left for 30 min at room temperature in the dark. The remaining DPPH was determined by the absorbance at 517 nm using a UV Spectrophotometer.

The radical scavenging activity (RSA) of the PCL/VE fibers was calculated as the percentage of DPPH radical inhibition according to Equation (1):

$$RSA\% = (1 - \frac{A_{sample}}{A_{control}}) \times 100 \quad (1)$$

where A_{sample} represents the absorbance of the sample solution and $A_{control}$ represents the absorbance of DPPH solution without the addition of the fibers.

3. Results

Vitamin E is a viscous liquid at room temperature and its addition to the PCL solutions prepared in 1,2-dichloroethane lead to a reduction in viscosity as shown in Figure 2. Despite these reduced viscosities electrospinning of Poly(ε-caprolactone) of micro scale fibres was easily achieved using the procedure described above as shown in Figure 3; the formation of fibres was nothindered by the inclusion of up to 17 wt% of Vitamin E, though the micrographs shown in Figure 3 suggests that the solidification is slower or less complete. It may be that the vitamin E phase separates from the polymer however, there was no evidence of any loss of Vitamin E in the fibres. Thus, 1H NMR analysis of the electrospun fibres using CDCl3 as a solvent, showed the presence of Vitamin E at the same quantitative levels as in the starting electrospinning solutions as shown in Figure 4.

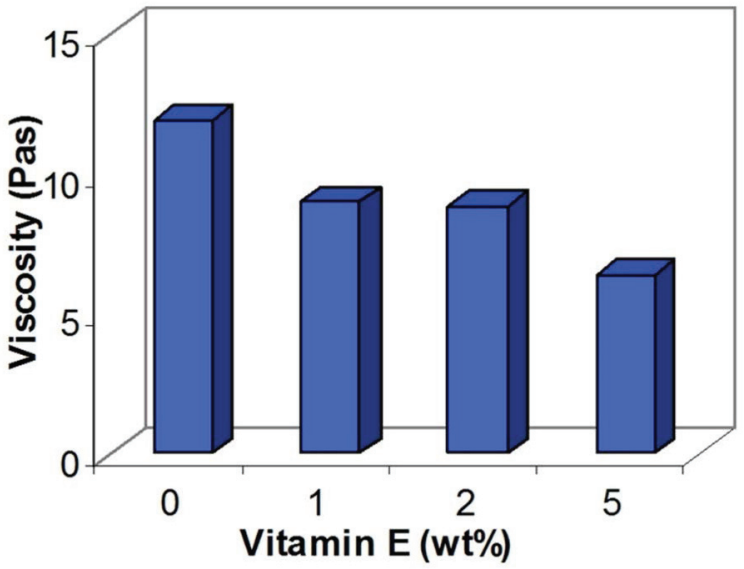


Fig. 2: Viscosities of the PCL/VE solutions in DCE as a function of the Vitamin E

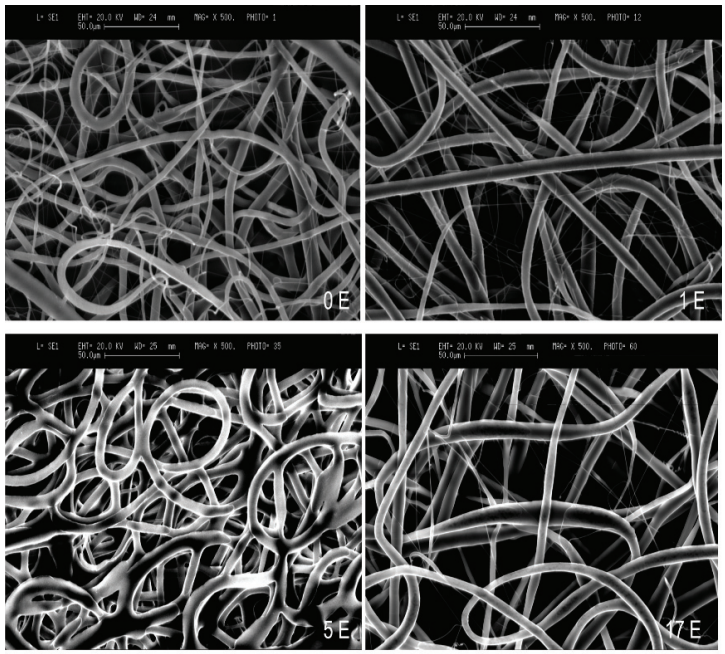


Fig 3. a) SEM micrographs of electrospun PCL fibres containing 0% Vitamin E, 1% Vitamin E , 5% Vitamin E and 17% Vitamin E

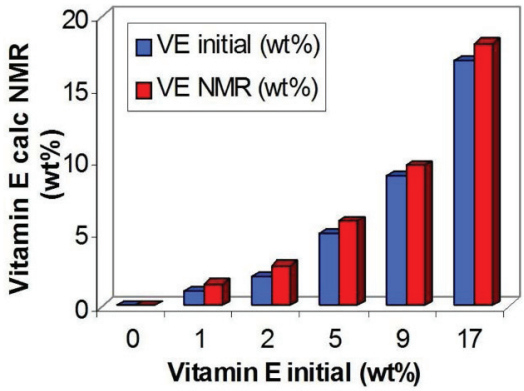


Fig. 4: Vitamin E content in the electrospun fibres compared to the composition of the feedstock solution

The results of the anti-oxidant activity obtained using the approach described in 2.3 are presented in Figure 5. It can be noticed that at low concentrations of Vitamin E in the microfibers, the effectiveness of the additive is not high but at higher concentrations most of the content is active as an antioxidant. The 10% of vitamin E which is not active presumably lies deep in the PCL fibres. This issue could be circumvented by preparing smaller diameter electrospun fibres but this could then impact on the life time of the anti-oxidant behaviour.

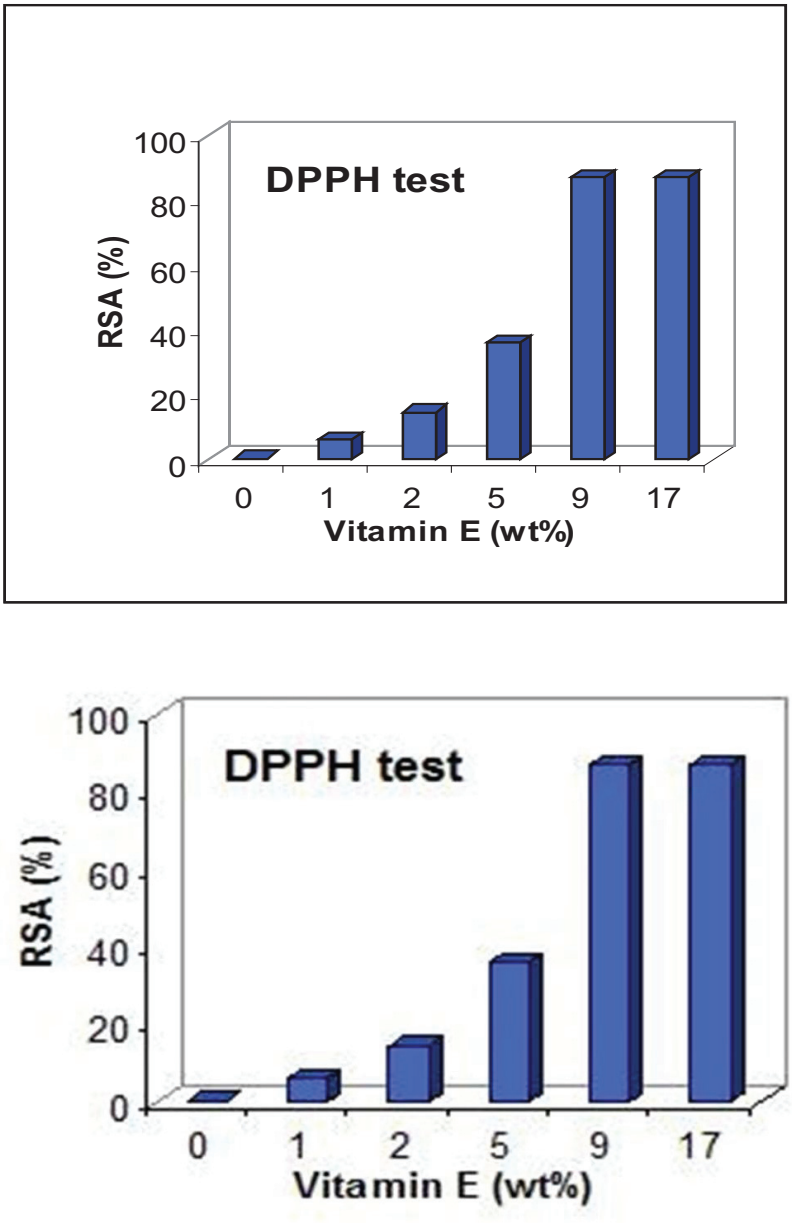


Fig. 5: Radical scavenging activity (RSA) of the PCL/VE fibers as a function of the Vitamin E content

As a final test of our design of anti-oxidant films we electrospun PCL/Vitamin E fibres on to a widely used common packaging film to identify if there were any problems with adhesion of the electrospun fibres to the polyolefin based barrier film. The films produced in this way had a significantly improved functionality with good adhesion of the antioxidant layer to the barrier film.

4.Conclusions

Electrospun fibres of microscale diameters were obtained from PCL/vitamin E solutions. At room temperature Vitamin E is liquid and the viscosity of the solutions reduced with increasing Vitamin E content. In fact the viscosity was ~ 50 % lower for PCL solutions containing 5 wt% Vitamin E compared with solutions without Vitamin E 1H NMR analysis showed that the Vitamin E is present at quantitative levels in the electrospun fibres obtained.

The enhanced antioxidant effect of the electrospun fibres containing Vitamin E was clearly demonstrated as the Vitamin E was accessible and effective as an antioxidant. The high surface area of the electrospun fibres provides a facile accessibility of the oxygen to the Vitamin E.

Acknowledgements

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